# THE SIGNIFICANCE OF THE "MERCURINIUM ION" IN OXYMERCURATION[1]

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Abstract

The complex formed by mercuric nitrate with cyclohexene seems not to resemble similar argentous, cuprous, and platinous salt complexes, since it is stabilized by nitric acid while they are decomposed by acidic media. Furthermore, the cyclohexene – mercuric nitrate – nitric acid system is not stable as are the others in absence of air but decomposes to yield two equivalents of mercurous salt and one equivalent of formylcyclopentane. One or both of these products are presumed to be the material which earlier workers by implication defined as 1-hydroxy-2-nitratomercuricylohexane. It has now been found that this product could not have been formed under the reaction conditions used by these earlier workers. Finally the solubilization of cyclohexene in aqueous mercuric nitrate, on which the earlier workers based their concept of an alkene-mercurinium ion, does not have its counterpart in the solubilization of cyclohexene in aqueous mercuric acetate, since the rate of solution in the latter case is not faster than the rate of hydroxymercuration. In consequence there is no present evidence that such an ion is involved in oxymercuration of alkenes.

On the basis of their studies of the system: mercuric nitrate – nitric acid – water – cyclohexene, Lucas, Hepner, and Winstein (7) have concluded that a mercurinium ion (I) and/or a hydroxymercurinium ion (II) is present in this system.
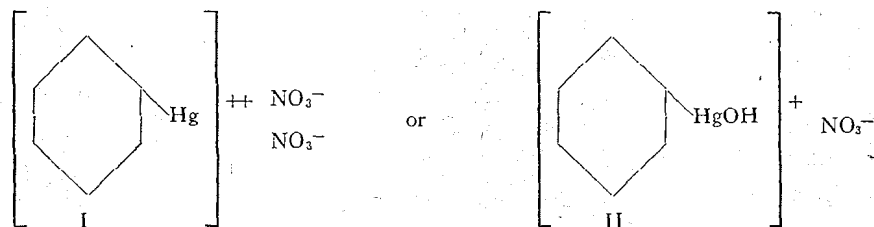
Furthermore they consider these ions are functional in the reaction known as oxymercuration.

These authors have arrived at this conclusion on the basis of an elaborate quantitative phase distribution study in which they made various adjustments because of "secondary reactions" that were especially prominent at low acid concentrations. They did not evaluate these "secondary effects" qualitatively but enumerated them as follows:

1. Over a period of time the apparent mercury concentration, determined by thiocyanate titration, decreased a few per cent per hour at the start and some 27% in 13 hr.

2. Over a period of time the apparent amount of unsaturation is within experimental error of the theoretical for about one and one-half hours and then

increases at an accelerating rate so that it is some 3% high after three hours and some 40% high after 17 hr. The unsaturation was determined by bromide-bromate titration as presumptive for cyclohexene.

3. Acidity increased with time.

4. After a time a solid separated from the mixture, especially at low acid concentrations. They considered that this material was probably 1-hydroxy-cyclohexane-2-mercuric salt (IV) which was derived via the mercurinium ion I or II.

Hydroxymercurials of cyclohexane (IV) have recently been prepared by us from cyclohexene (3). On the basis of observed second-order kinetics, stereo-chemical considerations, and the observation that methoxymercuration is faster than hydroxymercuration the ionic intermediate of Lucas, Hepner, and Winstein was considered less plausible as a mechanistic explanation than an intermediate molecular coördination complex (III) of cyclohexene with basic mercuric acetate.
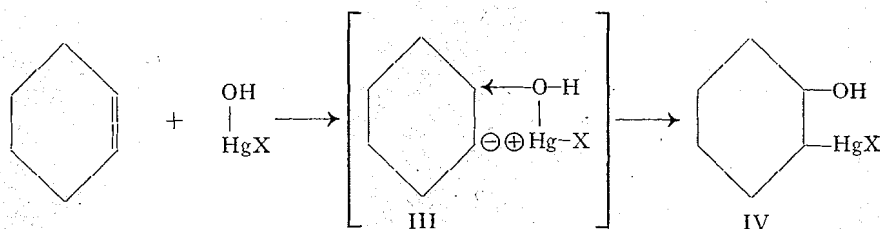
In view of this difference of opinion it seemed worthwhile to examine whether 1-hydroxy-2-nitratomercuricyclohexane (IV, X = NO$_3$) would be stable in the environment where the mercurinium ion is supposed to exist.

Since easy interchangeability of X in the —HgX substituent is characteristic of oxymercurials such as IV, it was unnecessary to prepare 1-hydroxy-2-nitratomercuricyclohexane. The known 1-hydroxy-2-acetoxymercuricyclo-hexane was added instead to solutions of nitric acid in water. The concentration range of 0.04–0.55 mole per liter used by Lucas, Hepner, and Winstein was examined. After a few minutes the homogeneous solutions were poured into aqueous sodium chloride solutions from which the analogous chloro-mercurial (IV, X = Cl) would be precipitated almost quantitatively (3). In every case when nitric acid was present the odor of cyclohexene was apparent, thus indicating decomposition of the oxymercurial. The results in Table I show that the mercurial could not have been formed in appreciable amount under these reaction conditions.

Thus hydroxymercuration with mercuric nitrate is not a significant reaction in water. However, it is interesting to note that methoxymercuration of cyclo-hexene may be accomplished with mercuric nitrate in methanol to give an 80% yield of 1-methoxy-2-chloromercuricyclohexane after the initial product is

TABLE I

SOLUTION OF 1-HYDROXY-2-ACETOXYMERCURICYCLOHEXANE
(0.09 MOLE PER LITER) IN DILUTE NITRIC ACID AFTER 10 MIN.

Expt. No.	Conc. HNO$_3$ mole/liter	Yield of IV X = Cl	
		gm.	%
1	None	0.29	97
2	0.079	0.02	7
3[a]	0.159	0.01	3
4	0.159	0	0
5	0.248	0	0
6	0.397	0	0

[a] *0.095 mole per liter of sodium nitrate added.*

treated with aqueous sodium chloride. Evidently the lesser activity of nitric acid in the alcoholic reaction medium, as contrasted to the activity in water, is responsible.

Since it is evident from these experiments that the solid observed by Lucas, Hepner, and Winstein could not have been an oxymercurial of type IV (X = NO$_3$) we carried out experiments approximating their reaction conditions at concentrations shown in Table II in order to examine this solid.

TABLE II

MOLAR CONCENTRATIONS YIELDING MERCUROUS SALT IN ONE HOUR

Conc. Hg(NO$_3$)$_2$	Conc. HNO$_3$	Conc. C$_6$H$_{10}$	% HgCl
0.050	0.050	0.042	4
0.050	0.100	0.042	2
0.095	0.275	0.033	4.5
0.200	0.55	0.275	11.5

After one hour the interface between the carbon tetrachloride and aqueous phases contained a small amount of solid which was found to be mercurous chloride. The presence of this salt seemed not to be owing to impurities since purified reagents were used, nor was the extent of reduction affected by the presence of atmospheric oxygen. Its chloride moiety probably originated by slight hydrolysis of the carbon tetrachloride.

When the aqueous layer was treated with sodium chloride, from 2–12% of the total mercury was precipitated as mercurous chloride. The decrease in apparent mercury concentration and slow increase in acidity reported by Lucas, Hepner, and Winstein may therefore be explained simply by the fact that mercurous nitrate cannot be titrated quantitatively by thiocyanate and that acid is necessarily formed during the reduction. Likewise the increase in apparent unsaturation may be expected since the bromide-bromate reagent will oxidize mercurous nitrate quantitatively to the mercuric state.

In order to ascertain the nature of the oxidation product corresponding to the reduction of mercuric salt we carried out an experiment at 25°C. using equimolar quantities of cyclohexene, mercuric nitrate, and nitric acid and omitted the carbon tetrachloride used by Lucas, Hepner, and Winstein. At no time was the odor of cyclohexene absent, but the nonaqueous phase disappeared after six minutes of violent shaking, and it reappeared after four hours, together with a small amount of solid and a characteristic disagreeable odor. This regenerated phase was removed after 16 hr. by azeotropic distillation under reduced pressure, leaving behind the solid.

Examination of the distillate showed that the nonaqueous phase comprised about half of the cyclohexene used initially, as well as formylcyclopentane in yield of about 37 mole % of the cyclohexene consumed. The actual yield of formylcyclopentane is slightly higher than this, because the nondistillable solid is the trimer of formylcyclopentane. This trimer has previously been reported as a polymer by Tiffeneau in a private communication relating to his report on formylcyclopentane (10) and later as a polymer of somewhat lower melting point (12). It can be formed from the aldehyde by treatment with 85% phosphoric acid, and it gives the same 2,4-dinitrophenylhydrazone. Since analysis with methyl Grignard reagent in the Kohler machine shows that it contains no active hydrogen or carbonyl group, we designate it as 2,4,6-tri-cyclopentyl-1,3,5-trioxane.

After the aqueous phase was chloroform-extracted to remove the trimer it was poured into aqueous sodium chloride. After the precipitate was extracted with methanol to remove a small amount of mercuric salt the remainder was found by its X-ray diffraction powder pattern to be essentially pure mercurous chloride in a molar yield of 90% of the mercuric nitrate used initially. The remaining 10% of mercuric salt is found in the methanolic extract and in the aqueous filtrate. When the mercuric salt is converted to the sulphide a few per cent of cyclopentanecarboxylic acid can be extracted from the aqueous filtrate. Under the conditions used in this experiment the reaction was rapid, since an aliquot removed after the first 20 min. showed that 10% of the mercuric salt was reduced to mercurous nitrate within this time.

The mechanism of this oxidation is at present obscure. The comparative consumption of reagents indicates that two molecules of mercuric nitrate are consumed per molecule of cyclohexene. None of the nitric acid is reduced to nitrous acid, but when insufficient mercuric nitrate remains in the system metallic mercury is precipitated. One might presume that the oxidation would produce either epoxycyclohexane or cyclohexandiol-1, 2 (*dl, ld* or *dd, ll*) and that one of these would undergo a Wagner–Meerwein type of 1, 2-rearrangement in the resultant solution. However, none of these substances shows any tendency toward rearrangement either in mercuric nitrate – nitric acid solutions or in similar solutions of mercurous nitrate.

The 1, 2-rearrangement of cyclohexandiol to formylcyclopentane has been reported as a pyrolysis over aluminum oxide (11) but these rearrangements

have not been effected in water solution. On the other hand, Tiffeneau (10) has found that 2-iodocyclohexanol on treatment with silver nitrate is converted to formylcyclopentane. Although he does not define his reaction conditions, these are fixed approximately by the fact that he obtained cyclohexyl nitrate (together with cyclohexene) by treatment of cyclohexyl iodide with silver nitrate.

Since Tiffeneau's rearrangement thus seemed to proceed through the nitrate ester we have prepared the mono- and di-nitrate esters of dd, ll-1, 2-cyclohexandiol, but find that neither of these shows any tendency to rearrange to formylcyclopentane. We have as yet been unsuccessful in our attempts to esterify dl, ld-1, 2-cyclohexanediol with mixed nitric-phosphoric acid.

Discussion

In view of the extent to which the oxidation reaction occurs with the reagent concentrations used by Lucas, Hepner, and Winstein one may inquire as to why their evaluated equilibrium ratios (K_E) should have been sufficiently constant that they were able to average 2/3 of their results instead of extrapolating to zero time. Inspection of their equation, simplified by the fact that cyclohexene is almost insoluble in water,

$$K_E = \frac{\text{Conc. } C_6H_{10} \text{ in aqueous phase}}{\text{Conc. } C_6H_{10} \text{ in } CCl_4 \text{ [initial conc. Hg}- \text{ conc. } C_6H_{10} \text{ in aq. phase]}}$$

shows, however, that it is a function only of the relative concentrations of cyclohexene in the two phases. The oxidation reaction may be expressed by the equation

$$C_6H_{10} + 2Hg(NO_3)_2 + H_2O \longrightarrow C_6H_{10}O + 2HgNO_3 + 2HNO_3$$
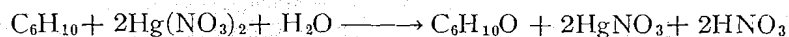
Now it is evident by actual inspection of the reaction mixture without carbon tetrachloride that cyclohexene forms a complex with mercuric nitrate in the aqueous phase at a rate depending on the initial concentration of the mercuric salt. Lucas, Hepner, and Winstein assigned 20 min. for this establishment of equilibrium between the two phases. During this time, and subsequently, the cyclohexene in the aqueous phase would be consumed, but this would not be apparent by titration with bromide-bromate because the formation of 2 molecules of mercurous nitrate would compensate equivalently for the loss of cyclohexene. Compensating transfer of cyclohexene from the nonaqueous layer would be minimized by the consumption of mercuric nitrate with which it would otherwise form a complex in the aqueous solution. Fortuitous constancy would thus be obtained. However, K_E eventually would decrease because consumption of mercuric nitrate at twice the rate for that of cyclohexene would decrease the amount of initial complex and thus redistribute the cyclohexene into the nonaqueous phase.

On the basis of their results, Lucas, Hepner, and Winstein have defined the complex comprising mercuric nitrate, nitric acid, and cyclohexene as a mercurinium ion, although none of the criteria for authentic ions (electrolytic

migration, abnormal depression of freezing point, etc.) were applied. Perhaps they did not mean an ion in the commonly accepted chemical sense, but rather a dipolar salt. However, they do consider the absorption of cyclohexene by aqueous mercuric nitrate as analogous with that of aqueous silver nitrate (7, p. 3102; 13) and presumably, with alkene-platinous halide (1, 5, 6, 9) and with alkene-cuprous halide complexes (8). But these complexes all have one common characteristic which would, indeed, seem necessary for complex cation formation: the complex forms with the lower valence state of the element. Thus olefins reversibly form complexes in neutral aqueous solution with argentous but not with argentic salts, with cuprous but not with cupric salts, and with platinous but not with platinic salts. One might then expect mercurous but not mercuric salts (since no higher valence is known) to form complexes with olefins. Actually undissociated complexes of alkenes with neutral mercurous salts have been observed (4).

Another significant difference between the argentous, cuprous, and platinous-alkene complexes and the mercuric nitrate – cyclohexene complex is found in the behavior toward acids. Although the former tend to decompose as the concentration of the acid is increased, the formation of the mercuric nitrate – alkene complex is enhanced by addition of nitric acid. Assuming that the acid is functioning to prevent the hydrolysis of mercuric nitrate, it is reasonable to assume that coordination occurs with the nitrato group. Decomposition of the resulting complex in presence of excess mercuric nitrate would result in the reaction products which have been isolated if the organic fragment were to rearrange to formylcyclopentane.
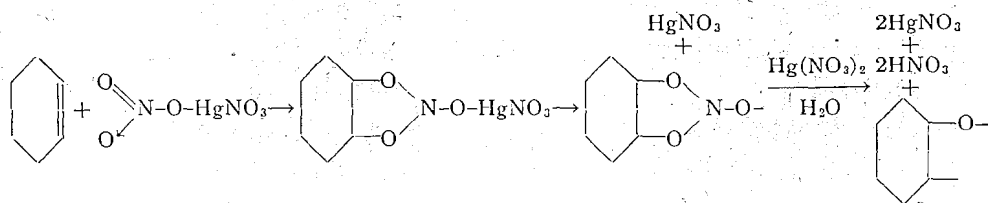
The nitrato group must be involved specifically in both the solubilization and oxidation process, since a 0.16 molar solution of mercuric chloride in 0.16 molar hydrochloric acid will not absorb a detectable amount of cyclohexene. This situation is unaltered when the acid concentration is increased tenfold or decreased to zero, although in the latter case the concentration of mercuric salt must be decreased in order to prevent its partial precipitation. This failure of mercuric chloride to form a complex with cyclohexene might be thought by some to be owing to its low degree of ionization. However, no such difficulty is encountered in coördination of mercuric chloride with tertiary amines, nor does the limited ionization of cuprous chloride prevent the mutual solubilization of the solid salt and the alkene in water (8).

The significance of the cyclohexene – mercuric nitrate – nitric acid complex, whether or not it be considered as a mercurinium ion, in oxymercuration is

doubtful. Firstly it has been shown in this report that no oxymercurial is produced under conditions favorable for the complex. Secondly in a system such as cyclohexene – mercuric acetate – water, where hydroxymercuration occurs almost quantitatively, there is no evidence for an intermediate complex consisting of these components. If such a complex were significant to the oxymercuration reaction then its rate of formation would have to be faster than that of the hydroxyalkane-mercurial, but this seems not to be the case.

Thus visible evidence for the formation of the cyclohexene – mercuric nitrate – nitric acid complex is provided by the solubilization of the alkene into the aqueous phase. If disappearance of the nonaqueous phase is used as a criterion, the formation of 1-hydroxy-2-acetoxymercuricyclohexane is complete in 13 min. when 0.01 mole quantities of mercuric acetate and cyclohexene are shaken in 250 ml. of water. On the other hand, 30 min. are required before the second phase disappears when 0.1 mole of acetic acid is included in an otherwise identical experiment. The yield of 1-hydroxy-2-chloromercuricyclohexane was 50–63% when both reaction systems were poured into dilute aqueous sodium chloride.

If the cyclohexene – mercuric acetate – water system had behaved analogously with that comprising cyclohexene, mercuric nitrate, and water, the solubilization of the alkene ought to have been accelerated by addition of acid. Instead it was retarded. Actually this diminution in rate is in accord with the concept that basic mercuric acetate reacts directly with the alkene to form the hydroxyalkanemercurial, since the concentration of basic salt would be reduced by presence of acid. Furthermore it is improbable that a stable ionic intermediate is operative since the rate of solution of the alkene closely approximates the rate of formation of the oxymercurial.

While there is thus no evidence that an alkene – mercuric salt complex is involved in oxymercuration the oxidation reaction is frequently encountered. However, it is ordinarily slower than oxymercuration in water or methanol. It does not interfere except during rate studies with alkenes which alkoxymercurate quite slowly. In such cases the precipitation of mercurous acetate from the alcoholic medium coincides with the decay of the rate constant. There are certain cases (2) such as the treatment of *trans*-stilbene with mercuric acetate in absence of catalyst where oxidation to 1, 2-dimethoxy-1, 2-diphenylethane is the exclusive reaction. In this instance addition of peroxides will sufficiently accelerate the oxymercuration so that it takes precedence over the oxidation, but boron trifluoride evidently accelerates both reactions, since dimethoxydiphenylethane is the only product obtained. The difference in function of these two catalyst types is the basis of a study presently carried out in this laboratory.

Experimental*

Stability of 1-Hydroxy-2-acetoxymercuricyclohexane in Dilute Nitric Acid.

Freshly prepared 1-hydroxy-2-acetoxymercuricyclohexane (0.32 gm., 0.0009 mole) was added to 9 ml. of water containing various amounts of nitric acid

* *All melting points have been corrected against reliable standards.*

(Table I) and the whole made up to 10 ml. volume with water. The compound dissolved after shaking for one minute. After 10 min. the whole was poured into dilute aqueous sodium chloride. The 1-hydroxy-2-chloromercuricyclohexane was filtered, dried, and weighed. In one experiment sodium nitrate was added to effect conversion to the nitratomercuri compound.

Methoxymercuration of Cyclohexene with Mercuric Nitrate

Experiments 1, 2, and 3 were carried out with 0.015 mole mercuric nitrate and 0.02 mole cyclohexene in methanol–water volumes of 50:0; 25:25, and 5:45 ml. respectively. A trace of nitric acid was added as catalyst. The times after which no mercuric oxide was precipitated by alkaline treatment of a test portion were respectively six, three, and nine minutes. The yields after 15 min. (80, 70, and 10% respectively) were estimated from the precipitate of *trans-1-*methoxy-2-chloromercuricyclohexane obtained by pouring the reaction mixtures into aqueous sodium chloride. The products from Expts. 1 and 2 both melted at 113–114°C. The product from Expt. 3 was very impure, but a single crystallization from acetone showed that it was partly 1-methoxy-2-chloromercuricyclohexane, m.p. 112–114°C.

Reaction of Cyclohexene with Aqueous Mercuric Nitrate – Nitric Acid Solution

A solution of 81.2 gm. (0.25 mole) of mercuric nitrate and 15.7 ml. (0.25 mole) of 70% nitric acid in 500 ml. of water was treated with 25 ml. of freshly purified cyclohexene containing only a trace of peroxide. After three minutes' shaking less than half the cyclohexene remained; there was no separate phase after six minutes. The odor of cyclohexene prevailed throughout the reaction. No difference in results was obtained when the reaction was carried out under nitrogen. At the end of 20 min. a test portion, removed, extracted with ether, and treated with aqueous sodium chloride precipitated mercurous chloride equivalent to 0.1 of the original mercury content. The ether extract gave a positive carbonyl test with dinitrophenylhydrazine.

A separate phase separated after four hours. After 16 hr. the reaction mixture was distilled under 15 mm. pressure into an ice-cooled receiver and then into a trap cooled by dry-ice. The aqueous residue (200 ml.), containing an oily phase, was twice extracted with 30 ml. portions of chloroform. A test of the extracted aqueous residue with alkali did not indicate any mercuric ion. Treatment with 60 ml. of saturated aqueous sodium chloride gave a white precipitate which was filtered, washed with methanol, and when vacuum dried, weighed 52.8 gm. Since this solid was shown to be pure mercurous chloride by test with alkali and by its X-ray diffraction pattern it represents 89.5% of the total mercury introduced into the reaction. The methanol used to wash the white precipitate was diluted with water and nitric acid, and then was treated with hydrogen sulphide. The mercuric sulphide which precipitated was washed with methanol. Its weight, 5.83 gm., represents 10% of the mercury originally used.

The chloroform extract was evaporated to leave a gummy solid, which was crystallized wastefully from ether – petroleum ether (b.p. 40–60°C.) mixture.

It weighed 0.25 gm. and melted at 123.5–124.5°C. When crystallized from hot 95% ethanol it melted at 128.5–129°C. When 70 mgm. of this compound was boiled with an equal amount of 2, 4-dinitrophenylhydrazine in ethanolic hydrochloric acid it formed the 2, 4-dinitrophenylhydrazone of formylcyclopentane, m.p. 163–164°C. after crystallization from boiling ethanol (30 ml. per gm.). Calc. for $C_{12}H_{14}N_4O_4$: C, 51.9; H, 5.05; N, 20.1%. Found: C, 51.8; H, 5.07; N, 19.9%.

The content of the dry-ice trap used in the vacuum distillation was dried with magnesium sulphate and distilled. The fraction, b.p. 81–83°C. weighed 9.2 gm. It was proved by methoxymercuration to be pure cyclohexene, which thus constitutes a 45% recovery of this starting material. The residue from this distillation was combined with the ether – petroleum ether liquors from which the solid, m.p. 124°C., was obtained, and also with an ether extract (dried with magnesium sulphate) of the aqueous distillate from the vacuum distillation. The accumulated oil was distilled to yield 4.45 gm., b.p. 80–81°C. (124 mm.), d_4^{20} 0.932, n_D^{20} 1.4428 and 0.8 gm. boiling approximately at 65°C. (8 mm.), n_D^{20} 1.4563. The first fraction, evidently formylcyclopentane, represents 37% of the cyclohexene consumed. The higher boiling fraction was redistilled at 215–216°C., corr., n_D^{20} 1.4532. Since these constants conform with those reported for cyclopentanecarboxylic acid, the crude yield is 5.6%.

The formylcyclopentane was redistilled, b.p. 133–134°C., n_D^{20} 1.44211, d_4^{20} 0.927. A portion was converted to the semicarbazone in 60% yield, m.p. 123–123.5°C. after crystallization from water. A third portion of the aldehyde was treated with 2, 4-dinitrophenylhydrazone in aqueous-ethanolic sulphuric acid. It yielded a dinitrophenylhydrazone the melting point of which was not depressed by admixture with the derivative described above.

2, 4, 6-Tricyclopentyl-1, 3, 5-trioxane

When 0.01 gm. of 85% phosphoric acid was allowed to flow into 0.20 gm. (0.002 mole) of formylcyclopentane solidification commenced at the interface. After two hours the solidification was complete. The solid was crystallized from boiling ethanol (25 ml. per gm.), m.p. 122.4–122.7°C., wt., 0.13 gm., or 65% of the theoretical yield. Recrystallization from the same solvent raised this melting point to 128–129°C. A mixed melting point with the solid compound obtained from the oxidation reaction was not depressed. The molecular weight determined by the Rast method initially gave a value of 292 (calculated 294) but this number decreased to 204 after repeated melting. Analysis in the micro-Kohler machine with methylmagnesium iodide showed absence of active hydrogen and carbonyl groups. Calc. for $C_{18}H_{30}O_3$: C, 73.5; H, 10.2%. Found: C, 73.5; H, 10.3%.

Reaction of Cyclohexene in Carbon Tetrachloride with Mercuric Nitrate and Nitric Acid in Water

A 250 ml. separatory funnel fitted with a sleeve-sealed stirrer was filled with 25 ml. of carbon tetrachloride and 200 ml. of water containing cyclohexene,

mercuric nitrate, and nitric acid in concentration shown in Table II. The remaining air-space was negligible and results were identical when the funnel had previously been swept with nitrogen. After one hour of violent stirring the nonaqueous layer was drawn off together with a small amount of mercurous chloride. The aqueous layer was run into centrifuge jars containing 100 ml. of saturated aqueous sodium chloride. After 10 min. the centrifugate was filtered and the white precipitate washed with methanol until it no longer gave a test for mercuric chloride. It was then dried at 110°C. and weighed.

Absorption of Cyclohexene by Aqueous Mercuric Acetate

To a solution of 3.16 gm. (0.01 mole) of mercuric acetate in 250 ml. water at 25°C. was added 1 ml. (0.01 mole) of cyclohexene. The whole was shaken for 13 min., until the cyclohexene layer disappeared. The liquor was poured into 50 ml. of saturated aqueous sodium chloride. The 1-hydroxy-2-chloromercuricyclohexane which precipitated weighed 2.1 gm. or 63% of the theoretical amount.

The experiment was repeated except that the volume of 250 ml. was made up from water and 5.7 ml. (0.1 mole) of acetic acid. Thirty minutes of shaking elapsed before the nonaqueous phase disappeared. The yield of 1-hydroxy-2-chloromercuricyclohexane was 1.67 gm. or 50% of theoretical. In neither case was more than a trace of mercurous salt detected. In either reaction mixture the amount of product remaining in the aqueous solution was found to be 23–25% of that actually isolated.

Aqueous Mercuric Salts with Cyclohexene

When 1 ml. of cyclohexene was shaken for 24 hr. with 50 ml. of an aqueous solution 0.16 molar both in mercuric chloride and hydrochloric acid less than 1% of the cyclohexene was absorbed. This behavior was the same when the acid concentration was increased to 1.6 N. The absorption of 1 ml. of cyclohexene was likewise not measurable in 100 ml. of 0.08 molar aqueous mercuric chloride without any acid.

When the turbid solution of 6.50 gm. (0.02 mole) of mercuric nitrate in 50 ml. of water was shaken over five minutes with 1.6 ml. (0.02 mole) of cyclohexene the solution gradually became clear but only 35% of the cyclohexene layer disappeared; after 10 min. solution was complete. After 20 min. the solution was poured into aqueous sodium chloride and the mercurous chloride filtered off, washed with water, methanol and ether. It weighed 0.75 gm. or 16% of the theoretical yield for complete reduction of the mercuric salt.

When 8.2 gm. (0.1 mole) of cyclohexene was shaken for 10 min. under nitrogen with a solution of 28.06 gm. (0.1 mole) of mercurous nitrate in 6.3 ml. (0.1 mole) of 70% nitric acid and 100 ml. of water a precipitate of mercury began to appear. There remained 6.06 gm. of cyclohexene or 74% of the original amount. When this experiment was repeated with inclusion of 0.1 equivalent of mercuric nitrate the precipitation of mercury was hindered for about one hour, and only 20% of the cyclohexene was absorbed.

Bromide-Bromate Titration of Mercurous Salt in Presence of Cyclohexene

The procedure of Lucas, Hepner, and Winstein (7) was followed in those runs where cyclohexene was present. In the absence of cyclohexene known amounts of potassium bromate and mercurous nitrate in dilute nitric acid were titrated with standard thiosulphate. Table III demonstrates the consumption of 1 equivalent of oxidizing agent by the mercurous salt or 2 equivalents by cyclohexene.

TABLE III

Expt. No.	Equiv. bromide-bromate	Equiv. HgNO₃	Equiv. unsaturation (0.5 equiv. C₆H₁₀)	Equiv. Na₂S₂O₃	Total calc. equiv. unsaturation
1	0.00392	0	0	0.00391	0
2	0.00366	0.00034	0	0.00332	0.00034
3	0.00366	0.00103	0	0.00262	0.00104
4	0.00366	0	0.00151	0.00218	0.00148
5	0.00366	0.00034	0.00151	0.00185	0.00181

Treatment of Cyclohexanediols and Epoxycyclohexane with Mercury Salts

When cyclohexene was replaced by either *cis* or *trans* cyclohexanediol-1, 2 or epoxycyclohexane in the acidified mercuric nitrate reagents and the reaction mixtures were extracted with chloroform after 24 hr. no trace of formylcyclopentane could be detected in the extracts. Similar results were obtained when acidified solutions of mercurous nitrate were treated with the same substances. Finally, 0.005 mole of these substances was each treated over several days with a solution of mercuric nitrite prepared by admixture of mercuric chloride and sodium nitrite. Some mercurous salt precipitated but no formylcyclopentane could be detected. The dinitrophenylhydrazine test reagent is very sensitive for detection of this aldehyde.

dd, ll-1-Hydroxy-2-nitroxycyclohexane

To a solution of 11.2 gm. (0.1145 mole) of 1, 2-epoxycyclohexane in 110 ml. of anhydrous ether at −70°C. was added over one hour 4.8 ml. (0.1145 mole) of 100% nitric acid. The solution was stirred an additional half-hour, then let warm to 25°C. and washed with water and then with 2% aqueous sodium carbonate until the aqueous wash water was neutral. After drying with magnesium sulphate the solution was distilled finally at 3.5 mm. to give a main fraction, b.p. 100–105°C. weighing 10 gm. This 55% yield was redistilled at 100°C. (3 mm.), n_D^{20} 1.47892, d_4^{20} 1.225. M_D (calc.) 37.2; found 37.4. Calc. for C₆H₁₁NO₄: C, 44.6; H, 6.93; N, 8.71%. Found: C. 44.5; H, 7.02; N, 8.63%.

dd, ll-1, 2-Dinitroxycyclohexane

To a mixed acid prepared from 2.88 ml. (0.068 mole) of 100% nitric acid and 2.76 ml. (0.048 mole) of 96% sulphuric acid stirred and maintained at 0°C. was added 3.00 gm. (0.026 mole) of *dd, ll-1*, 2-cyclohexanediol over 30 min.

After 15 min. longer at 0°C. the whole was drowned in ice water which was then ether-extracted. The ether extract, washed with water and sodium carbonate until neutral and dried with magnesium sulphate, was distilled finally at 0.5 mm. to yield 2.2 gm. (65%) b.p. 100–102°C. This was redistilled at 118–118.5°C. (5.5 mm.) n_D^{20} 1.47555, d_4^{20} 1.318. M_D calc. 44.1; found, 44.0. Calc. for $C_6H_{10}N_2O_6$: C, 34.9; H, 4.86; N, 13.6%. Found: C, 35.1; H, 4.88; N, 13.5%.

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